

AN ECO-FRIENDLY APPROACH TO SYNTHESIS AND CHARACTERIZATION OF MAGNETITE (Fe₃O₄) NANOPARTICLES USING *PLATANUS ORIENTALIS* L. LEAF EXTRACT

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Nowadays, different plant materials are utilized to bio-synthesize nanoparticles by using green technology mainly due to having no harmful chemicals. Although much research has been placed on the bio-based materials for the synthesis of the nanoparticles, there is a need to explore different perspectives and in detail process conditions with characterizations. This study dealt with the synthesis of the Fe₃O₄ nanoparticles using an environmentally friendly technique by aqueous ferric chloride hexa-hydrate and ferrous chloride tetra hydrate with 2/1 molar ratio and sodium hydroxide using leaf water extracts, which act as an efficient stabilizer and capping agent simultaneously. For this purpose, the leaves of *Platanus Orientalis* L. plant were used. To the best of our knowledge, it is the first time that this plant was used to synthesize the magnetite nanoparticles. One of the most important techniques to understand the hydrodynamic radius on an ensemble average size of the nanoparticles is zetasizer technique. It was demonstrated that the size of the synthesized nanoparticles was around 34.72 ± 6.77 nm. In addition, several complementary analytical techniques were employed to characterize the magnetite nanoparticles including zeta potential measurements, TEM, UV-Vis, FTIR, TGA, and XRD methods.

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1. Introduction

Biosynthesis methods demonstrated many advantages over other classical synthesis procedures due to the availability of more biological entities and eco-friendly procedures. The rich biodiversity and easy availability of plant entities have been highly explored for the nanomaterials and their syntheses [1-5]. The biologically synthesized nanomaterials have potential applications in various areas such as treatment, diagnosis, targeted drug delivery, development of surgical nano-devices, magnetic resonance imaging, and commercial product manufacturing [6-9].

Magnetic nanoparticles are basically nano-dimensional materials that can respond to the magnetic field. There is a growing interest on the synthesis and characterization of magnetic nanoparticles due to their superior functions in various applications [9, 10]. The presence of magnetic characteristics as well as easy and safe synthesis of the nanoparticles in the laboratory environment increase the utilization of the materials in the different application fields and get noticeable consideration among the scientists. The main purpose of green synthesis research is to improve a synthesis method for obtaining the environment friendly, non-toxic, superparamagnetic and low cost magnetic nanoparticles [11-13].

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The biological syntheses of nanoparticles by different macroscopic or microscopic organisms such as plant extracts, bacteria, fungi, seaweeds, yeast and microalgae have recently gained an interest [14-20]. The biosynthesized nanomaterials can effectively control the various endemic diseases with less adverse effects. Plants contain various abundant phytochemicals such as carboxyl, hydroxyl, and amino functional groups [21]. In the recent studies, many plants were employed for the nanoparticle production, e.g. *Centella asiatica*, *Murraya koenigii*, *Alternanthera sessilis*, *Padina pavonica* (Linnaeus) and *Thivy*, and so on [22-32].

The purpose of this study was to improve the synthesis method for obtaining magnetic nanoparticles (Fe_3O_4) by using ferric chloride hexa-hydrate, ferrous chloride tetra-hydrate and by extraction of *Platanus* leaves without any stabilizers, distributors and oxidants. By this way, an easy, economic and environmentally friendly synthesis was aimed without using organic solvents and physical steps with surface active materials. The obtained magnetic nanoparticles were characterized using transmission electron microscopy (TEM), fourier transform infrared spectroscopy (FT-IR), zeta potential measurements, ultraviolet–visible spectroscopy (UV–Vis), thermogravimetric analysis (TGA), and X-ray diffraction (XRD) methods.

2. Experimental section

2.1 Preparation and Extraction of Plant Leaves

Fresh plant leaves were collected in the city of Eskisehir, Turkey. Then, they were washed for removing dust and any impurities by using distilled water and dried under the room temperature. The plant leaves (1 g) were extracted by boiling water (100 mL) in 250 mL glass flasks for 5 minutes. Then the resulted yellow colored extract was cooled to the room temperature and filtered with whatman filter paper before centrifuging at 2000 rpm for 2 minutes to remove any heavy biomaterials. Finally, the extract was kept at 25 °C in order to be used for the synthesis of the target magnetic nanoparticles.

2.2 Synthesis of Magnetic Nanoparticles

The synthesis of the magnetic nanoparticles was carried out by an improved biosynthesis method. To do so, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (Sigma-Aldrich) and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (Sigma-Aldrich) at 1/2 molar ratio were dissolved in 80 ml water by stirring at the speed of 700 rpm for 2 h. Thereafter, plant leaves extract was added to the metal ions solutions. After the addition, the color of the solution started to change in a short time from yellow to black. The color change represents the formation of nanoparticles which can be seen in Figure 1. Then, 1.0 M of NaOH solution was added to the metal ion solution until the pH value was attained to 11 [30]. The specimens were filtered to remove the solid product and washed by ethanol. Finally, the specimens were dried in an oven at 50 °C and prepared for the characterization.

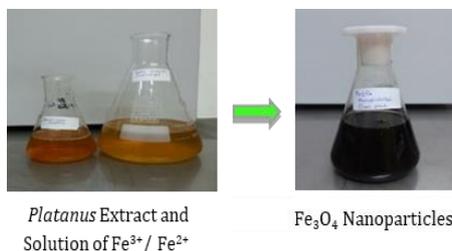


Fig. 1. Images for the synthesis of the magnetite nanoparticles using *Platanus* leaf extract

2.3 Characterizations of the Nanoparticles

2.3.1 Transmission Electron Microscopy

TEM analyses of the synthesized magnetite nanoparticles were taken by JEOL-1220 on an accelerating voltage of 80 kV. The TEM method was used to observe the shape, morphology and

size of the magnetic nanoparticles. The nanoparticles were prepared on carbon coated copper of TEM grids.

2.3.2 X-ray Diffraction

The synthesized magnetite nanoparticles were evaluated by a PANalytical Empyrean operating at 45 kV/40 mA using Cu K α radiation ($\lambda = 1.54059 \text{ \AA}$) with angular range from 5 to 80° (2θ) under nitrogen flow rate that was set to 2 mL/min.

2.3.3 Fourier Transform Infrared Spectroscopy

An ATR-FTIR analysis method was applied by using Spectrum 100 Optica Spectrometer between 4000 - 500 cm^{-1} . To obtain the spectrum, the analysis sample was placed on the diamond crystal and then the data of FTIR spectrum was recorded.

2.3.4 Particle Size and Zeta Potential Measurements

Nano ZS zetasizer (Malvern Instruments, UK) was employed to determine the hydrodynamic particle sizes and zeta potential of the nanoparticles.

2.3.5 Ultraviolet–Visible Spectroscopy

UV-vis spectroscopic studies were carried out to verify the biosynthesis of the magnetic nanoparticles by the absorption maxima of wavelength of 200–600 nm on Perkin-Elmer Lambda 35 spectrophotometer.

2.3.6 Thermogravimetric Analysis

Thermogravimetric analysis (TGA, SII Exstar 6000) was used to observe the behavior of the iron oxide nanoparticles by weight loss in the determined temperature ranges. The nanoparticles were heated from the room temperature to 700 °C with a heating rate of 10 °C/min under nitrogen atmosphere.

3. Results and discussion

3.1 Magnetic Property

To investigate the magnetic properties, the synthesized nanoparticles were placed next to a magnet as shown in Figure 2. It can be realized that the produced nanoparticles displayed their magnetic properties when exposed by the magnetic field. This preliminary test proved that the synthesized particles demonstrated the magnetic properties. Then, this test was repeated under recording the time as seconds to find out the movement of the particles in aqueous solution. The average particles' mass movement is very fast. In about seven seconds almost all of the particles moved toward the magnet as observed by the naked eyes.



Fig. 2. Observation of the magnetic properties of the nanoparticles before (left) and after (right) placing the magnet

3.2 Transmission Electron Microscopy

Fig. 3 demonstrates the TEM images of the nanoparticles in order to observe the morphologies and size distributions of the magnetite nanoparticles. The average size of the

magnetite iron oxide nanoparticles synthesized with *Platanus* leaf extract was calculated by using Image J program (National Institutes of Health, USA). As the TEM images show, there are roughly two different average particles sizes. The geometry of the most nanoparticles was quasi-spherical like structures with the average diameters of 7.69 ± 1.55 nm. The resulted size of the nanoparticles is smaller than those of the particles produced in many previous studies [25-32]. Other particles possess the average diameter of 39.70 ± 2.76 nm. The smaller nanoparticle sizes are more dominant than the large ones as the TEM image shows clearly. The reason of the variety of the size distribution of the nanoparticles could be because of the mixture of various derived components with different reducing properties in *Platanus* leaf extract [31]. Recently, Rao et al. [29], Machado et al. [34], and Yuvakkumar et al. [35] reported the nanoparticles with size ranges of 100-200 nm, 15-45 nm and 100-200 nm, respectively. Another important point is that the nanoparticles did not have any considerable aggregation based on the TEM images.

In this study, the smallest size of the nanoparticles which we obtained was about 3 nm. So far the smallest magnetite nanoparticles synthesized by the green methods can be ascribed to the citrine juices extract with approximately 3 nm [36]. It indicates that we have successfully achieved to obtain the similar diameter range by using a different plant and method for the first time.

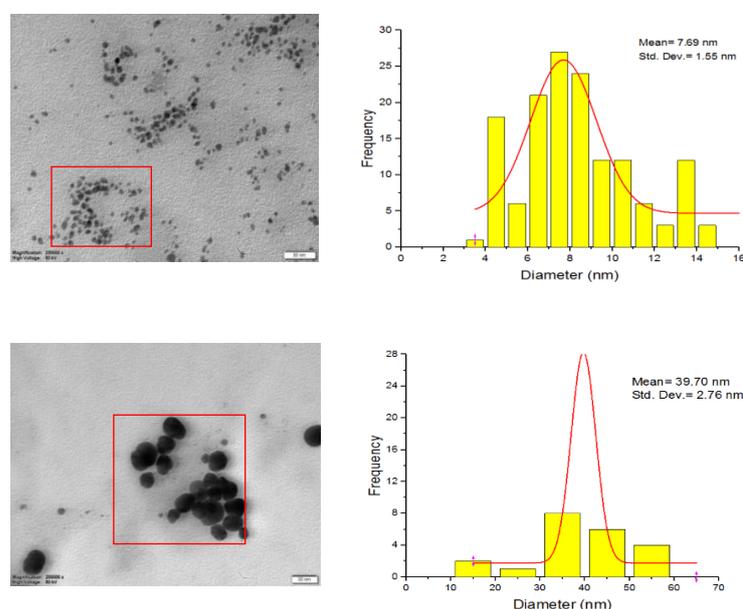


Fig. 3. TEM images and size distributions of magnetite iron oxide nanoparticles

3.3 X-ray Diffraction

The XRD analysis determined the crystalline structure of the synthesized magnetite nanoparticles by the characteristic peaks as shown in Figure 4. It is found that all the reflection peaks at (2 0 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1), (4 4 0), and (5 3 3) can be indexed by the cubic inverse spinel structure of the magnetite iron oxide nanoparticles [34-35]. Yew et al. [15] reported similar XRD pattern for the nanoparticles using *Kappaphycus alvarezii* extract. The reflection peak positions and relative intensities can be well matched with the standard magnetite of Fe_3O_4 . The crystal size of the nanoparticles was evaluated using the Debye-Scherrer equation ($D = K\lambda/\beta\cos\theta$) on the basis of the (311) line [39-40] where D is the mean particle size, K stands for the Scherrer constant, λ as wavelength of X-ray radiation source (Cu-K α irradiation), β shows the full width at half maximum (FWHM) value of the diffraction line and θ is half diffraction angle (Bragg angle). Using the equation, the estimated crystallite size of the synthesized magnetite iron oxide nanoparticles was about 12.3 nm. It also should be indicated that the Debye-Scherrer equation always tends to underestimate the real crystallite size [41].

The XRD analysis determined the crystallite size of the nanoparticles to be 12.3 nm, which was well coincided with the result obtained from the TEM that demonstrate a size distribution between 3 and 60 nm as seen in Fig. 3.

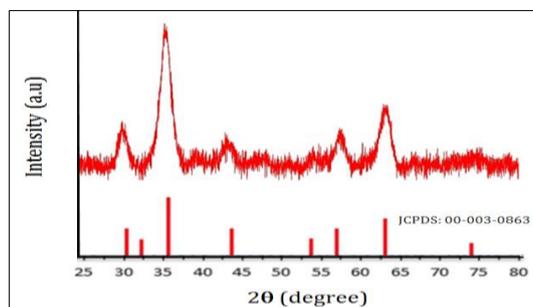


Fig. 4: XRD pattern of nanoparticles synthesized with *Platanus* leaf extract.

3.4 Fourier Transform Infrared Spectroscopy

Figure 5 shows the FTIR spectra of *Platanus* leaf extract. The spectra of the obtained nanoparticles in the solution revealed the absorption bands at 3270, 2925, 1632, 1373, 1031, and 553 cm^{-1} as shown in the Figure. The broad peak at 3270 cm^{-1} in the nanoparticles solution demonstrated the O-H stretching vibration of carboxylic acids, alcohols and phenols [42-43]. The weak peaks at 2925 cm^{-1} can be ascribed to the C-H stretching vibrations of the methyl group [44]. The strong absorption peak of 1632 cm^{-1} is due to the C=C aromatic ring stretching vibration. The absorption peak at 1373 cm^{-1} can be assigned to bending vibration of C-H of methyl group. The strong peak at 1031 cm^{-1} was contributed to the C-O-C stretching and O-H in *Platanus* leaf extract. One remarkable peak was seen at 553 cm^{-1} in the spectra of the synthesized magnetite nanoparticles [18]. This peak is assigned to the Fe-O stretching band of the bulk magnetite. The metal-oxygen band at 553 cm^{-1} can be contributed to intrinsic stretching vibrations of metal at the tetrahedral site [45]. Yew et al. and Yuvakkumar et al. reported FTIR peaks for the synthesized magnetite nanoparticles using *Kappaphycus alvarezii* and *Rambutan* extracts with 556 nm and 545 nm, respectively [18, 46]. The FT-IR results confirm and strongly suggest that the presence of polyphenols act as capping agent and efficient stabilizer for magnetite nanoparticles in the solution.

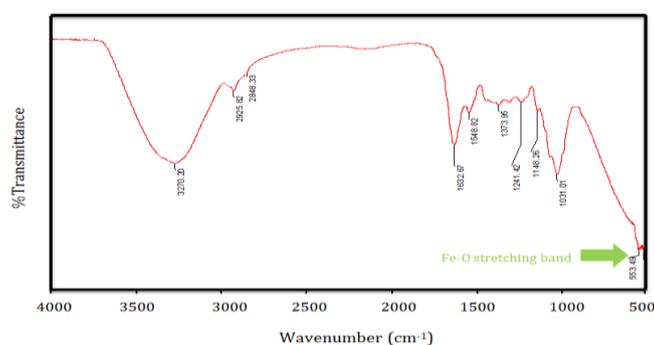


Fig. 5. FTIR graph of the synthesized magnetite nanoparticles by using *Platanus* leaf extract

3.5 Particle Size and Zeta Potential Measurements

Magnetite nanoparticles that were synthesized by the leaves' extract displayed high negative zeta potential values. Therefore, they demonstrated stability under a wide pH range [47]. On the other hand, the negative zeta potential value of the nanoparticles at the neutral pH represents the negative surface charge due to hydrolysis of the surface metal ion. When particle size is 12.5 nm, the surface charge value is less than -20 mV and for 90 nm nanoparticles size it is

-10.5 mV which indicates a remarkable decline in the zeta potential with larger size, while the surface charge value is positive even for 7.0 nm α -Fe₂O₃ nanoparticles due to proton absorption site variations and specific surface area [48-52]. In this investigation, the average size of the magnetite nanoparticles synthesized by our eco-friendly method was determined as 34.72 ± 6.77 nm and the stability of the magnetite nanoparticles was examined by the measurement of zeta potential that its value was -24.80 mV as shown in Figure 6. Therefore, we can conclude that the nanoparticles are highly stable when synthesized using *Platanus* leaf extract.

Because of the various surface charge mechanisms and particle size distribution, the further small intensity peaks appear in the zeta potential graphic [49]. This study shows that the nanoparticles do not have any variety in surface charge mechanisms and the particle size distribution.

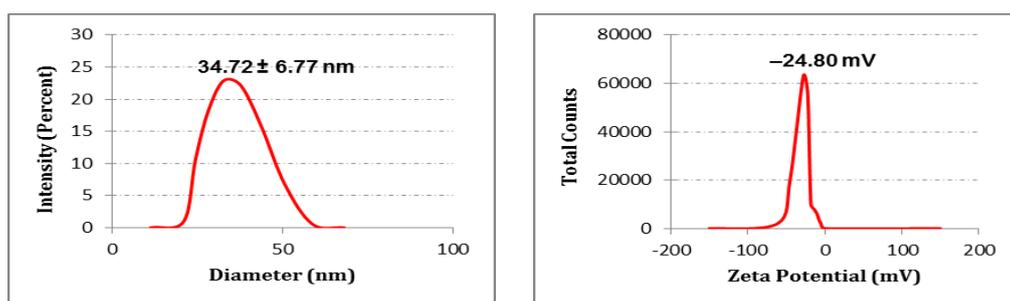


Fig. 6. Average particle size and zeta potential of the magnetite nanoparticles.

3.6 Ultraviolet–Visible Spectroscopy

To confirm the formation and stability of the particles, UV-vis spectral analysis was carried out by using the aqueous colloidal solution. The UV–Vis spectrum of the nanoparticles indicated the absence of the absorption band at 280 nm and 373 nm as shown in Figure 7. Awwad et al. [44], and Meyyappan et al. [53] reported respective maximum absorption values at 233 nm and 303 nm for the magnetite nanoparticles synthesized using *Carob* leaf and *Desmodium gangeticum* root extracts, respectively. In this study, the observed changes in the maximum absorption may be due to the oxidizing agent [54] and nanoparticle size [55] which can change nanoparticle stabilization.

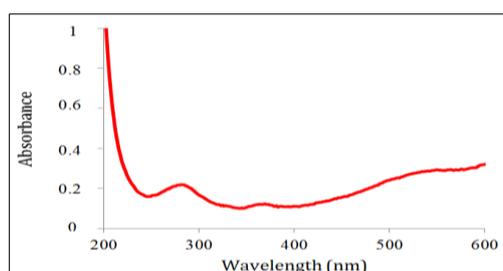


Fig. 7. UV–vis spectra (absorbance vs wavelength) of the magnetite nanoparticles

3.7 Thermogravimetric Analysis

Figure 8 shows the thermogravimetric analysis (TGA) results of magnetite nanoparticles in which two weight loss values were observed. The first weight loss is between 30 and 100 °C and the second is between 100 and 400 °C. The initial weight loss can be attributed to the dehydration of the samples, and the second weight loss is ascribed to the decomposition of the *Platanus* leaf extract. The decomposition of the *Platanus* leaf extract as capping agent occurred at temperature of 400 °C completely and did not show any major change till 700 °C. The dehydration of the

nanoparticles and other possible particles were about 7.5 %, while the decomposition of the *Platanus* leaf extract was about 14.5 %.

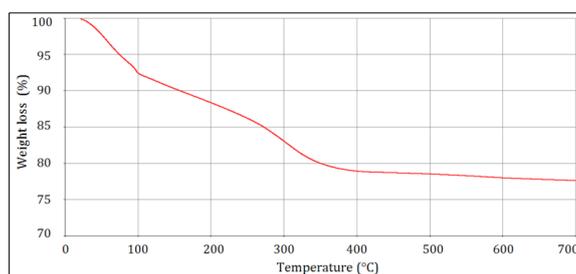


Fig. 8. TGA curve of the nanoparticles

4. Conclusions

The Fe₃O₄ magnetite nanoparticles were successfully obtained by using a simple environment friendly technique from the selected natural plant extracts. To do this, *Platanus* leaf extract was utilized instead of the chemical and organic solvents to produce the magnetite nanoparticles. Our synthesis approach demonstrated several important outcomes. These can be summarized as:

- The XRD analysis proved that the resulted Fe₃O₄ nanoparticles have high-purity crystalline form.
- The FTIR spectroscopy indicated the presence of the nanoparticles peak at 553 cm⁻¹.
- The TEM results showed that most of the particles had quasi-spherical like structures.
- The zetasizer revealed the average diameter of the nanoparticles with particle size of 34.72± 6.77 nm.

As a result, our eco-friendly technique for synthesizing the nanoparticles is simple and low cost, and it can be carried out using non-toxic components, and hence it has a high potential to use in many different applications from wastewater treatment to biomedical uses.

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